

PRELIMINARY ENGINEERING DATA FOR SCALE UP
OF A BIOMASS VACUUM PYROLYSIS REACTOR

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INTRODUCTION

The thermal decomposition of wood into charcoal and tar is an old process. One example of the existing technology for wood carbonization is the Lambiotte process. The ATOCHEM plant located in Premery, France, is based on the principle of external gas circulation and is a completely continuous process (1). The heating gas moves upward in the retort and constantly releases its heat into the wood, which is moving downward. The annual wood charcoal production of this plant is nowadays 20 000 t. The charcoal finds its use in the barbecue and the iron industries. Another example is the Brazilian beehive kiln for charcoal production in a batch mode. In Brazil, charcoal is mainly sold to the iron, the cement and the barbecue industries. In 1986, the total annual production of wood charcoal in Brazil was 7.5×10^6 t (2).

The recovery of by-products is important for the economy of both processes. The French recover high-value chemicals such as food aromas from the pyrolytic liquors (3). The Brazilians market the wood tar by-product as a bunker fuel oil (4). However, further studies are still needed and are being conducted by the industry in order to make a greater and a better use of the tar and oil fraction.

Laboratory (5) and Process Development Unit (6,7) studies originally conducted at the Université de Sherbrooke, and now conducted jointly with the private industry at the Université Laval, have led to the conclusion that thermal decomposition under reduced pressure is an attractive approach for the conversion of biomass into chemical and fuel products. This approach is characterized by low pressure and short residence time of the vapor products in the reactor. When compared with conventional, atmospheric pressure carbonization, vacuum pyrolysis has the potential to significantly enhance the yields of organic liquid products with respect to solid and gaseous products. The pyrolytic oils obtained from this process can be deoxygenated into transportation fuels (8) and sugars (9) upon further upgrading. Specialty as well as rare chemicals can also be extracted from the oil product (10).

This paper discusses the preliminary engineering data leading to the construction of a vacuum pyrolysis pilot plant for the conversion of wood into oils, chemicals and charcoal.

EXPERIMENTAL

A schematic of the Process Development Unit (P.D.U.) used in this study is shown on Figure 1. The reactor is a multiple-hearth furnace 2 m high and 0.7 m diameter, with six hearths. Heat transfer is provided through heating elements.

At the onset of an experiment wood chips are poured batchwise in a hopper that sits on top of the reactor. The hopper is equipped with a feeding device and is hermetically sealed. For the experiments reported, 6 to 16 kg of wood chips with a granulometry 1/4" to 1/2" Tyler Sieves were fed at a constant rate of 0.8 to 4 kg h⁻¹.

A mechanical vacuum pump removed the organic vapor and gas products from the reactor through a series of outlet manifolds set along the reactor cylinder. Each outlet was connected to a heat exchanger where the vapors were condensed and recovered as liquid into individual glass receivers. Cold tap water circulating on the shell side of the exchangers was used as cooling medium. The vapors from the heat exchange units were collected in a train of receivers that served as a secondary condensing unit. The first receiver was immersed in a bath of a water-ethylene glycol mixture. Receivers 2 and 3 were immersed in baths of dry ice-acetone. Receiver 4 was filled with glass wool at room temperature.

Pressure in the system was lower than 80 mm Hg (absolute) under steady-state conditions. The noncondensable gas was continuously pumped into a 500 L vessel that was set under vacuum at the beginning of the run.

The solid residue was directed toward the bottom of the reactor. The residual charcoal was received in a metallic jar installed on a load cell.

At time zero of the run, wood chips were fed in the preheated reactor. The heating plate temperatures increased from top to bottom of the reactor. A typical temperature profile was 200 °C to 450 °C. The radial temperature gradient for any heating plate was lower than 5 °C during any single run.

The P.D.U. was attached to a central microprocessor that permitted simultaneous data acquisition and control of some 75 operating parameters (64 are recorded and 11 are controlled). Air leakage through the system was lower than 1.3×10^{-3} atm L s⁻¹.

The experiments conducted on the P.D.U. were performed with Populus deltoides. The 8-year-old fast-growing poplar clone D-38 was planted in Brockville, Ontario. The sample was essentially all sapwood with no bark. It was shipped to our laboratories in the form of chips by Forintek Canada Corp., Ottawa. Its elemental composition was determined to be 48.2% C, 6.4% H, 45.3% O, 0.09% N, and 0.05% S. Its gross heating value was 4660 kcal kg⁻¹ with an average ash content of 0.6%. Moisture of the air-dry feedstock was determined to be 5.9%.

RESULTS AND DISCUSSION

Yields and mass balance

Results for the operation of the multiple-hearth furnace at varying final thermal decomposition temperature and reactor pressure are presented in Table 1 of the paper. Oil, pyrolytic water, charcoal and gas yields are

presented along with the mass balance calculation for each run. Table 1 indicates that the largest amount of oil is obtained at the lowest pressure and the higher temperature conditions. The oil yield in particular drops sharply with even a slight increase in pressure. Table 1 also indicates that a reactor temperature in the range of 425 - 450 °C is optimum to get the maximum yield of oil from wood. Table 2 summarizes the data obtained for the gas phase composition for the different runs.

Separation of water from the organic liquid phase

One objective of the vacuum pyrolysis process is to produce large quantities of liquid fuels and chemicals from wood. However during the process the liquid organic product is mixed with water (moisture and pyrolytic water). Since extraction of chemicals or further processing of pyrolytic oils mixed with water is difficult and expensive, it is highly desirable to separate the bulk of the aqueous phase from the organic liquid phase.

The separation of water and the organics was achieved during this study by using a series of shell and tube heat exchangers with cool to warm water circulating in the shell section. This series of heat exchangers served as a primary condensing stage for the recovery of the liquid organic fraction. Water was primarily recovered in the series of traps that followed (see Figure 1). The relative proportion of water and oil in both condensing sections is shown in Table 3 of the paper. Table 3 indicates that the lower the pressure, the better the separation between oil and water (see runs C019 and C025). On the other hand at similar operating pressure, the lower the cooling temperature, the more efficient the recovery of oil in the primary condensing section (see runs C023 and C025).

Oil refining

Further fractionation of the wood oil product is necessary if the objective is to either recover pure chemical compounds, or upgrade or process specific chemical group components. Results which are reported by Renaud *et al* (8) and Pakdel *et al* (10) show that the multiple-hearth reactor can be operated in a mode that enables the separation and recovery of selected fractions of liquid fuels and chemicals.

Heat requirement for the pyrolysis reaction

Another engineering parameter to be considered when designing a full scale pyrolysis plant is the amount of energy required for the pyrolysis of each mass unit of wood fed to the reactor. Such value has been empirically determined using the P.D.U. described in this paper, and the detailed procedure has been published elsewhere (11). The determination was based on the difference of electric energy consumed before of after wood was fed to the reactor (heat loss to the atmosphere), and that of the electric energy required for maintaining the multiple-hearth furnace at predetermined set-point temperature with wood chips flowing through the reactor. It was concluded that the heat required for vacuum pyrolysis of aspen wood is about 134 kcal kg⁻¹ of anhydrous wood. Overall, the reaction is slightly endothermic.

Heat required for cooling the organic vapors

The amount of heat removed when cooling the organic vapor products at the primary condensing stage was also experimentally determined (see Figure 1). The heat exchange (Q_w) between the cooling medium (water) and the hot vapor products was calculated using the Equation 1.

$$\text{Equation 1)} \quad Q_w = mC_p (T_{w,in} - T_{w,out})$$

where m is the water flowrate, C_p is the heat capacity for water and $T_{w,in}$ and $T_{w,out}$ is the water temperature at the inlet and the outlet of the heat exchanger, respectively. After taking into account the heat loss to the atmosphere, the overall heat exchanged while cooling the gas and vapor product to 50 °C was found to be 112 kcal kg⁻¹ of air-dry wood.

The experimental set-up simultaneously enabled the calculation of the overall heat-transfer coefficient U for the heat exchangers. The data were plugged in Equation 2.

$$\text{Equation 2)} \quad Q_w = UA (\Delta T)$$

where A is the transfer area and (ΔT) is the temperature driving force. The calculations led to the conclusion that U values vary between 7 and 13 kcal h⁻¹ m⁻² °C⁻¹ according to the position of the heat exchanger attached to the multiple-hearth furnace (11).

Determination of standard heat of reaction

The equipment used enabled us to determine the standard heat of reaction for pyrolysis of air-dry wood chips. For matter of convenience the standard state for wood considered as "a pure substance" was 323 K (50 °C) and 12 mm Hg. The standard heat of reaction was calculated using the Equation 3.

$$\text{Equation 3)} \quad \Delta H^\circ_{323} = \Delta H^\circ_t - \Delta H^\circ_r - \Delta H^\circ_p$$

where ΔH°_r is the total enthalpy change for the reactants from temperature T to 323 K.

ΔH°_p is the total enthalpy change for the products from 323 K to temperature T

ΔH°_t is the enthalpy change for the three-step process including the enthalpy change during the isothermal reaction at 323 K.

Figure 2 illustrates how each term in Equation 3 was empirically determined during run CO23. ΔH°_r and ΔH°_p in Equation 3 were calculated using an average heat capacity of 0.5 cal g⁻¹ °C⁻¹ for wood and 0.246 cal g⁻¹ °C⁻¹ for wood charcoal. The value for ΔH°_{323} in Equation 3 was found to be 22 kcal kg⁻¹, which confirms that the reaction is slightly endothermic. Although this value has limiting practical use, it should be viewed as an attempt to improve our theoretical knowledge of thermodynamics of wood pyrolysis.

Calculation of thermal efficiency of the reactor system

The thermal efficiency of the system defined as the ratio of useful energy provided by the vacuum pyrolysis reactor, to the energy supplied to it during a specific period of operations, has been determined for the same experiment CO23. The calorific values of the end-products represented the following percentages of the heating value of the initial feedstock: wood

charcoal 36%, wood oil 41% and gas, 5%. Using these data together with values from Figure 2 enabled us to determine that the thermal efficiency was 82%. For this calculation the mechanical pump electric energy requirement was not considered and the reactor was assumed to be perfectly insulated.

Heat transfer phenomena in the reactor

In the pyrolysis reactor, heat can be transferred by conduction, by radiation and by convection. Heat transfer by convection is negligible due to the low pressure conditions in the reactor. Both conduction and radiation play a significant role during pyrolysis and the latter factor is increasingly important at higher temperature levels (12).

The overall heat-transfer coefficient was estimated using the general relation $Q = UA (\Delta T)$. For the multiple-hearth furnace used, the actual heat transfer area used was estimated to be approximately 30% of the total available surface (6 heating plates), since the wood chips moving bed didn't cover the entire section. The transfer area was estimated to be 0.4 m^2 . The temperature driving force was calculated to be $62 \text{ }^\circ\text{C}$ (logarithmic mean), with $25 \text{ }^\circ\text{C}$ and $437 \text{ }^\circ\text{C}$ for the temperature of incoming raw material and the exiting charcoal, respectively, and $200 \text{ }^\circ\text{C}$ and $450 \text{ }^\circ\text{C}$ for the temperature of the top and the bottom heating plate, respectively. With Q_w equal to 150 kcal kg^{-1} (air-dry wood), the overall heat-transfer coefficient was found to be equal to $22 \text{ kcal h}^{-1} \text{ m}^{-2} \text{ }^\circ\text{C}^{-1}$.

CONCLUSION

A multiple-hearth reactor has been successfully tested for the production of high yields of liquid fuels and chemicals. The reactor enabled the separation and recovery of water on the one hand and oil fractions or the other hand. Oil yields reached about 50% by weight of the air-dry feedstock.

Heat required for the pyrolysis of wood is slightly endothermic and was determined to be 134 kcal kg^{-1} (on an anhydrous basis). The standard heat of reaction at 323 K and 12 mm Hg was found to be approximately 22 kcal kg^{-1} of air-dry wood. The thermal efficiency of the process is high, in the range of 82%. The overall heat transfer coefficient in the reactor is about $22 \text{ kcal h}^{-1} \text{ m}^{-2} \text{ }^\circ\text{C}^{-1}$ which is in range with the existing commercial multiple-hearth furnaces. Preliminary theoretical calculations indicate that a significant reduction of the heat surface area of the reactor can be achieved by operating the reactor at a higher temperature zone in order to enhance the radiative effect.

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FIGURE 1 - SCHEMATIC OF THE VACLIN PYROLYSIS PROCESS DEVELOPMENT UNIT

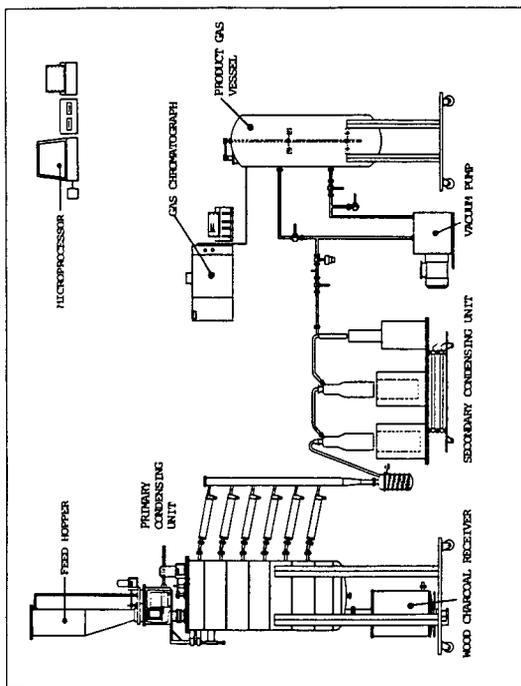


FIGURE 2 - MASS AND ENERGY BALANCES AROUND THE PYROLYSIS REACTOR

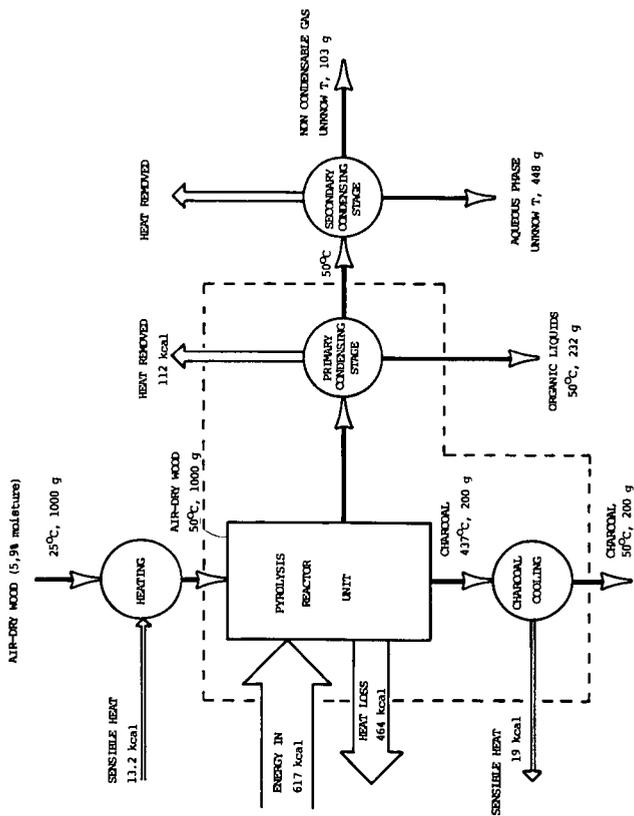


TABLE 1 - YIELDS AND MASS BALANCE FOR VACUUM PYROLYSIS OF WOOD IN A P.D.U.

RUN #	FINAL TEMPERATURE (°C)	REACTOR PRESSURE (mm Hg)	WOOD FEEDSTOCK (kg)	YIELDS (% wt. wood organic basis)				MASS BALANCE CLOSURE
				OIL	WATER	CHARCOAL	GAS	
0010	425	12	5.98	46.4	18.2	24.2	11.2	96.7
0012	363	18	5.99	41.6	14.9	33.0	10.5	97.5
0014	450	25	6.03	45.8	17.0	25.6	11.6	96.1
0015	425	14	6.00	50.1	15.2	25.0	9.7	96.3
0019	465	80	3.39	39.7	21.6	24.7	14.0	96.7
0023	450	12	15.43	50.9	16.5	21.3	11.3	98.3
0024	450	30	18.30	47.4	16.9	25.5	10.2	97.9
0025	450	10	15.99	50.0	15.6	23.0	11.4	98.6

TABLE 2 - GAS PHASE COMPOSITION DURING VACUUM PYROLYSIS OF WOOD IN A P.D.U.

RUN #	FINAL TEMPERATURE (°C)	REACTOR PRESSURE (mm Hg)	TOTAL GAS YIELD (% wt. wood organic basis)	GAS COMPOSITION (% wt.)					OTHERS*	CO/CO ₂
				CO ₂	CO	CH ₄	H ₂	C ₂ -C ₆ HYDROCARBONS		
0010	425	12	11.2	59.2	33.6	2.4	0.9	1.5	2.4	0.57
0012	363	18	10.5	60.4	34.9	0.9	0.1	0.9	2.8	0.57
0014	450	25	11.6	65.7	28.1	1.4	1.0	1.6	2.2	0.43
0015	425	14	9.7	63.8	30.5	1.5	0.8	1.3	2.1	0.48
0019	465	80	14.0	60.0	31.4	3.3	0.7	2.8	1.8	0.52
0023	450	12	11.3	60.7	31.6	2.7	0.0	1.4	3.6	0.52
0024	450	30	10.2	63.5	29.8	2.6	0.7	1.5	1.9	0.47
0025	450	10	11.4	64.6	30.3	1.9	0.4	1.0	1.8	0.47

* Others gases were among the followings : methanol, ethanol, acetone and acetaldehyde.

TABLE 3 - SEPARATION OF WATER AND PYROLYTIC OIL DURING CONDENSATION

RUN #	REACTOR PRESSURE	FINAL TEMPERATURE	COOLING TEMPERATURE (°C)	PRIMARY CONDENSING UNIT		SECONDARY CONDENSING UNIT		TOTAL LIQUIDS (kg)
	(mm Hg)	(°C)		OIL (%)	WATER (%)	OIL (%)	WATER (%)	
0019	80	465	11-28	52.2	19.2	7.4	21.2	2.06
0023	12	450	50-55	32.2	1.5	36.7	29.6	10.45
0024	30	450	30-35	39.8	1.6	27.2	31.4	11.85
0025	10	450	15-20	47.8	3.4	27.2	21.6	10.53